

Multi-Scale Monitoring and Prediction of System Responses to Biostimulation

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I. INTRODUCTION AND MOTIVATION

To advance solutions needed for remediation of DOE contaminated sites, approaches are needed that can elucidate and predict reactions associated with coupled biological, geochemical, and hydrological processes over a variety of spatial scales and in heterogeneous environments. Our previous laboratory experimental experiments, which were conducted under controlled and homogeneous conditions, suggest that geophysical methods have the potential for elucidating system transformations that often occur during remediation. Examples include tracking the onset and aggregation of precipitates associated with sulfate reduction using seismic and complex resistivity methods (Williams et al., 2005; Ntarlagiannis et al., 2005) as well as estimating the volume of evolved gas associated with denitrification using radar velocity. These exciting studies illustrated that geophysical responses correlated with biogeochemical changes, but also that multiple factors could impact the geophysical signature and thus a better understanding as well as integration tools were needed to advance the techniques to the point where they can be used to provide quantitative estimates of system transformations.

Our current research includes theoretical, numerical, and experimental investigations, performed at the laboratory and the field scales, to determine if geophysical methods can be used to uniquely monitor system transformations. Our work is geared toward the Uranium Mill Tailings site at Rifle, CO, site (Figure 1), where ERSP-sponsored investigations are exploring the efficacy of electron-donor amendments for facilitating sustainable microbial reduction of U(VI) to U(IV) through a series of local-scale field experiments conducted in 2002-2005 (Anderson et al., 2003; Vronis et al., 2005). Early experiments at the site showed that U(VI) loss from groundwater occurred synchronously with growth of *Geobacter* after acetate amendment, and illustrated the importance of maintaining iron-reducing conditions for optimal U(VI) removal. Since the interplay between iron and sulfate reduction is believed to be of critical importance to the sustainable reduction of U(VI) at this site, quantitative interpretation of geophysical data in terms of redox state, exhaustion of bioavailable iron mineral phases, or onset of sulfate reduction is expected to greatly benefit the understanding and sustained remediation of uranium at the site.

The sections below describe the key components of our work, including laboratory and field characterization and monitoring during biostimulation experiments that were conducted in 2006, reactive transport modeling, and biogeochemical property estimation using geophysical datasets.

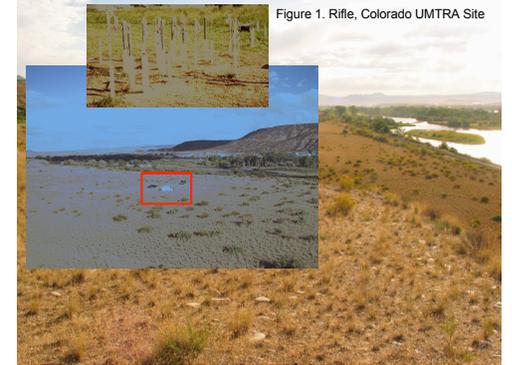


Figure 1. Rifle, Colorado UMTRA Site

II. RESEARCH METHODS

Our research includes theoretical, numerical, and experimental investigations performed at the laboratory and the field scale, which involve the remote monitoring and prediction of biogeochemical processes using geophysical methods and reactive transport modeling, respectively. Linkage between the laboratory-scale and field-scale investigations will be ensured by using the same (native) sediments (and in some cases, groundwater), and by using the same geophysical measurement techniques and reactive transport code at both scales. By investigating the geophysical response to coupled processes and by performing calibrated and validated reactive transport modeling at both scales under the same environmental conditions, we are beginning to investigate how novel monitoring and modeling approaches scale with space and time.

KEY COMPONENTS

Laboratory Experiments



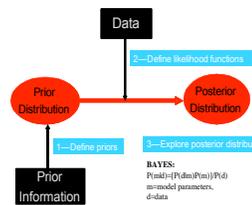
Laboratory studies are being performed to mimic experimental conditions at the Old Rifle, CO, field site using native groundwater and sediments. Radar, seismic, SP, and complex resistivity measurements are being collected during the experiment concomitant with geochemical, hydrological, and microbiological measurements. Experiments are investigating the responses of geophysical attributes to:

- Ferric Oxide Reduction during Biostimulation;

- Stimulation of natural microbial community in native Sediments under sulfate reducing conditions;
- Stimulation of natural microbial community in native sediments under sustained iron reducing conditions
- FeS Oxidation.

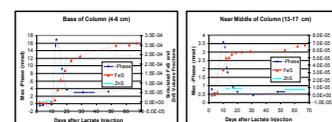
These experiments will indicate the potential of using geophysical measurements to remotely indicate when a system is undergoing iron or sulfate reduction.

Estimation Framework



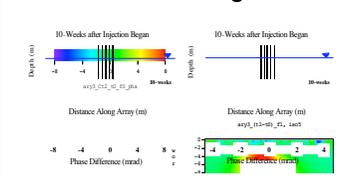
Our previous work has illustrated that time-lapse geophysical signatures track the onset and evolution of end-products associated with bioremediation, such as the production of iron sulfides (Williams et al., 2005). *A key component of this project is the development of a stochastic estimation framework that permits the quantitative estimation of properties associated with biogeochemical transformations.* The methodology is performed using a Markov chain Monte Carlo approach, and by using petrophysical models that link the geophysical attributes to biogeochemical properties. The model will be tested using data collected at the laboratory scale and then applied to time-lapse field geophysical data collected during biostimulation experiments.

Reactive Transport Modeling



This component focuses development and validation of reactive transport models at the laboratory and field scales. We are using the pore-water chemistry determined over the course of lab experiments and the solid-phase mineralogy determined via post mortem analysis to develop a defensible description of the reaction network (pathways and rates). The reactive transport modeling is carried out using CRUNCH (Steefel et al., 2003) and TOUGHREACT codes. *The reactive transport model is being calibrated to the geophysical data,* but only by using the independent constraints provided by the microbiological, chemical, and physical data. This is a key step, since the geophysical data will be crucial in developing a high-resolution data set at the field scale, where complete microbiological, chemical, and physical characterization of the subsurface material will not be feasible.

Field Characterization and Monitoring



Crosshole seismic, radar and complex resistivity, and SP data were collected this year between several well pairs and within all three flow cells at the Rifle Site. Comparison of the characterization data with borehole electrical, geological, and flowmeter logs and tracer data is being performed as a first step in *estimating hydrogeological heterogeneity at the field scale.* The time-lapse geophysical datasets, collected in association with the field-scale biostimulation experiments, are being interpreted in terms of *biogeochemical transformations.* Comparison of the characterization and monitoring datasets permits assessment of the *role of heterogeneity on system transformations.*

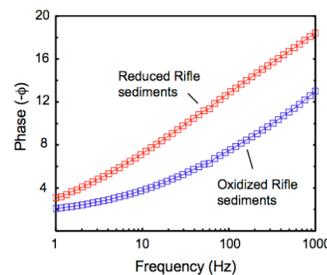
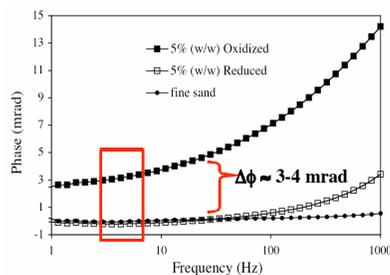
III LABORATORY EXPERIMENTAL RESULTS

Previous laboratory experiments in sandy materials with a single microbial strain illustrated that complex resistivity data can be used to detect the onset of sulfide production associated with sulfate reduction (Williams et al., 2005). Here, we expand upon this work by repeating the experiments using site-derived sediments and groundwater (and thus microbial community), and by also performing additional experiments aimed at investigating the geophysical transformations to biogeochemical transformations, such as:

- clay mineral alteration accompanying the reduction of structural ferric iron;
- oxidant end-products accompanying an increase in groundwater oxygen concentration, and
- reduction of structural iron in bulk sediments through exposure to sulfide-rich groundwater.

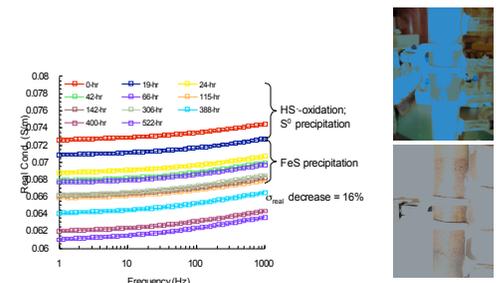
These studies, which are briefly described below, indicate that several of these processes should be detectable at the field scale.

Impact of Iron Reduction. For the first test, the clay-sized fraction (< 2-um) was isolated from the bulk sediments and reduced enzymatically using a site-isolated strain of *Geobacter*. The complex resistivity data revealed a slight decrease in both the phase response and the imaginary component of resistivity following bioreduction, suggesting that the alteration of clay minerals by microorganisms is capable of decreasing the polarization response of sediments containing iron-bearing phyllosilicates.



Phase impacts of oxidation. Comparison of the laboratory phase response of oxidized and reduced Rifle, CO sediments over the indicated frequency range. The sediments were obtained from an un-amended portion of the Rifle site from a depth approximately 4 to 4.5-m below ground surface, sieved to include the < 2-mm fraction, and saturated with site groundwater. For the reduced sediments, an extended 70-day *in situ* incubation was performed in the measurement cell using groundwater amended with 50-mM acetate. Over this time interval, extensive precipitation of FeS was documented having an acid volatile sulfide (AVS) concentration of 18-umol S²⁻ g⁻¹ sediment, in comparison to the oxidized sediment, which had a AVS concentration of 0.05-umol S²⁻ g⁻¹ sediment.

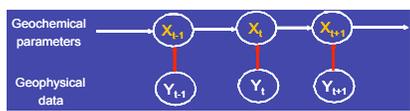
We also explored the **impact of oxidative and abiotic processes on the real component of resistivity** through the precipitation of low conductivity phases, such as elemental sulfur created through the oxidation of bisulfide by ferric iron present in crystalline iron (oxy)hydroxides. Oxidized aquifer sediments were added to sulfide-rich groundwater lacking a readily available source of acetate and the complex resistivity response was measured over the course of 2 weeks. During this time, the real component of conductivity (i.e. bulk conductivity) decreased by up to 16%, presumably as a result of the precipitation of S⁰ and/or disseminated, disordered FeS. Over the same time period, the polarization response increased significantly (44% at 10-Hz), most likely as a result of the precipitation of FeS and in agreement with our previous observations monitoring metal sulfide precipitation.



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IV. GEOCHEMICAL ESTIMATION FRAMEWORK

We have developed a stochastic framework that permits estimation of the evolution of end-products associated with biogeochemical transformations using time-lapse geophysical data and the petrophysical models described below. Both models include an error term (ϵ).



Seismic P-wave velocity (v_p) and attenuation ($1/Q$) as a function of precipitate radius (r) and volume (p) are represented using a patchy model (Pride et al., 2004).

$$\begin{cases} v_p(t_i) = g_1(p(t_i), r(t_i)) + \epsilon_1 \\ Q_1(t_i) = g_2(p(t_i), r(t_i)) + \epsilon_2 \\ m_n(t_i) = a_1 \left(\frac{p(t_i)}{r(t_i)} \right)^b + \epsilon_3 \\ \tau(t_i) = a_2 r(t_i)^2 + \epsilon_4 \end{cases}$$

Chargeability (m) and time constant (τ) are related to volume and mean grain size of evolved precipitates using a modified Cole-Cole model (Slater et al., 2006).

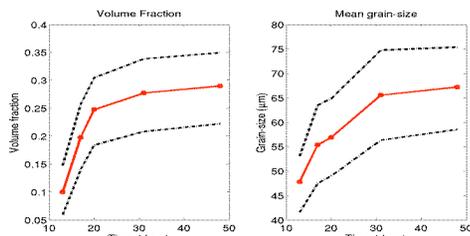
We have used a Markov chain monte carlo method for the estimation problem, which has been expressed in a Bayesian formulation. This approach permits updating of the prior information about geochemical parameters using the time-lapse geophysical data and the petrophysical models, which are expressed in terms of likelihood functions. The developed stochastic framework is general and flexible and can be used to combined various types of geophysical data for geochemical parameter estimation. Here, we have applied the method to the time-lapse seismic and IP datasets collected in association with the laboratory column experiments described by Williams et al. (2005) to estimate the evolution of the volume and mean grain size of sulfide precipitates.

$$f(\{p(t_i), r(t_i), i=1, n\}, \{a_1, a_2, b\})$$

$$\propto \prod_{i=1}^n \{f(m_n(t_i) | p(t_i), r(t_i), a_1, b) f(\tau(t_i) | r(t_i), a_2)\}$$

$$\prod_{i=1}^n \{f(v_p(t_i) | p(t_i), r(t_i)) f(Q_1(t_i) | p(t_i), r(t_i))\}$$

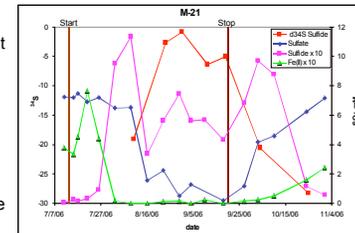
$$f(a_1) f(a_2) f(b) \prod_{i=1}^n f(p(t_i), r(t_i))$$



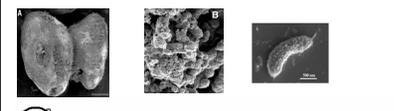
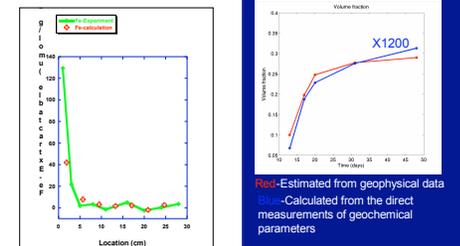
In this first attempt to use geophysical data to quantitatively estimate end-products associated with remediation, we find that geophysical data provides useful information about the onset and evolution of sulfide precipitates. As is describe in Section V, iteration of the advanced modeling and monitoring is being performed to improve both approaches.

V. ISOTOPE STUDIES & REACTIVE TRANSPORT MODELING

Isotope Studies. Sulfur isotopes of SO_4^{2-} and HS^- were analyzed in a background well and three down-gradient monitoring wells beginning near the onset of SO_4^{2-} reduction associated with the 2006 biostimulation experiment at the Rifle Site. Analysis of $\delta^{34}\text{S}$ of SO_4^{2-} and HS^- during in situ U(VI) bioremediation has indicated that variation in isotopic composition of sulfur species can be detected under these conditions. The data indicate a high level of fractionation between SO_4^{2-} and HS^- at both onset and recovery and minimal fractionation at the height of SO_4^{2-} reduction. These methods can therefore be applied as an indicator of the stage of SO_4^{2-} reduction, and may provide a more sensitive means of obtaining a timeline of these processes needed for the modeling effort. In addition, the data are useful determining the composition of incoming SO_4^{2-} , and the causes of aqueous HS^- depletion.



Modeling Studies. We are using the pore-water chemistry determined over the course of lab experiments and the solid-phase mineralogy determined via post mortem analysis to develop a defensible description of the reaction network (pathways and rates). The reactive transport modeling is carried out using CRUNCH and TOUGHREACT codes. The figure to the right shows that predictions of FeS and ZnS accumulation rates agree closely with those determined by 0.5 N HCl extraction measurements from column studies of Williams et al. (2005). The studies also suggest that the bacteria are highly motile and chemotaxis must be considered in the transport model.



Sand grains (600-800 μm)
 Aggregate cells (10-60 μm)
 Encrusted single cell (1-2 μm)
 Isolated precipitates (3-5nm)

Comparing Geophysical and Modeling Estimates. The estimates of evolved precipitates obtained using the time-lapse geophysical data were compared with those estimates obtained using the numerical modeling approach. We found that the time evolution profiles were very similar in shape, but different in mass balance by a factor of 1000. Our working hypothesis is that both methods give different information about the evolved precipitates: the geochemical modeling predicts the absolute volume of precipitates, whereas the geophysical methods are likely to sense the surface area that is impacted by FeS and ZnS secondary phases growing on grains or biomass. This observation suggests that a combination of geophysical monitoring and geochemical modeling may lead to new insights about the dynamic system.

VI. FIELD SCALE CHARACTERIZATION AND MONITORING

Through field characterization and monitoring using seismic, radar, complex electrical and SP measurements, and through coupling the field characterization with the lab-scale experiments and reactive transport modeling described above, we will investigate at the Rifle Site the following questions:

- Can geophysical data be used to distinguish between iron and sulfate reduction processes and track these process over space and time?
- What is the role of heterogeneity on the system transformations?

Characterization of subsurface hydrogeological heterogeneity is being performed across the Rifle Flow Cells using a combination of geologic logs, flowmeter data, tracer test, and electrical logs from wellbores together with radar, seismic, and electrical tomographic datasets. As characterization data were collected at different times in relationship to the manipulation experiments, a first step in the analysis is determining the value of the data for characterizing initial (i.e., unperturbed) hydrogeological conditions and for developing site-specific petrophysical relationships between the hydrological and geophysical attributes, as is shown by the figure to the right.

Preliminary analysis of the geological and geophysical datasets suggests that there is consistent layering across the Rifle study site and that this layering may impact transport and transformations.

Monitoring is also being performed using time-lapse complex resistivity, radar, seismic, and SP to image spatiotemporal changes in the system in response to biostimulation.

The figures to the right illustrate the complex resistivity responses associated with the 2006 biostimulation experiments, which were designed to facilitate iron reduction in the '2004' flow cell and sulfate reduction in the '2005' flow cell. Figure A illustrates where the surface datasets were collected relative to the two injection galleries. Figures B-C illustrate the inversion of the complex resistivity data relative to baseline conditions, while Figure D illustrates illustrates geochemical responses. The expected transformations associated with the 2004 & the 2005 experiments are shown below. Based on the 2005 and 2006 complex resistivity responses, which indicate the formation of iron sulfides, we interpret that a zone of mixing formed between the two injection areas.

2004 Injection Area: $\text{FeOOH}(s) + 3\text{H}^+ + e^- \rightarrow \text{Fe}^{2+}(aq) + 2\text{H}_2\text{O}$
 2005 Injection Area: $\text{SO}_4^{2-} + 9\text{H}^+ + 8e^- \rightarrow \text{HS}^-(aq) + 4\text{H}_2\text{O}$
 2006 Zone of mixing: $\text{Fe}^{2+}(aq) + \text{HS}^-(aq) \rightarrow \text{FeS}(s) + \text{H}^+$

The flow diversion from the 2005 to the 2004 flow cell may have been impacted by pumping activity as well as local heterogeneity. These field-scale geophysical responses:

- Are in agreement with the laboratory responses;
- Provide different information at different frequencies, which suggests that the geochemical estimation framework described in IV should be applicable to field datasets;
- Suggest that complex resistivity approaches are useful for identifying important changes in mineralogy associated with sulfate reduction at the field scale.

The figures to the right illustrate the use of borehole SP data to monitor transformations associated with the biostimulation experiment that was performed in 2006 at the Rifle Site. The figures illustrate that there is an excellent correlation between the SP response and the geochemical parameters, suggesting the usefulness for SP logging as a low cost means for estimating persistence of low redox conditions associated with sulfate-reduction.

This ongoing research suggests that field IP methods tend to be extremely sensitive to mineralogical transformations, while SP data are most sensitive to aqueous geochemical changes associated with remedial treatments.

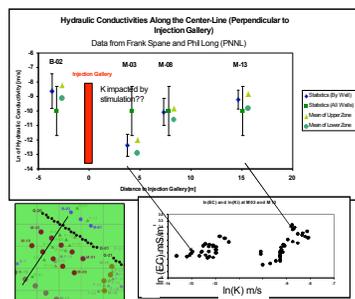


Figure A. Plan map of the injection galleries and monitoring well locations used during the 2006 Rifle, CO bioremediation experiment. Injection in the gallery labeled '2005' focused on long-term (~70-day) acetate amendment targeting sulfate-reduction, whereas the gallery labeled '2004' was used for a short-duration (~21-day) acetate amendment targeting iron-reduction; both amendment experiments ended on the same date. Surface-based complex resistivity data were acquired at three time-intervals during the amendment experiments along two lines, one located parallel and perpendicular to flow; the later was located approximately 1.5-m downgradient from the injection galleries. Data were acquired between 30 Cu/CuSO₄ electrodes equally spaced over a distance of 30-m.

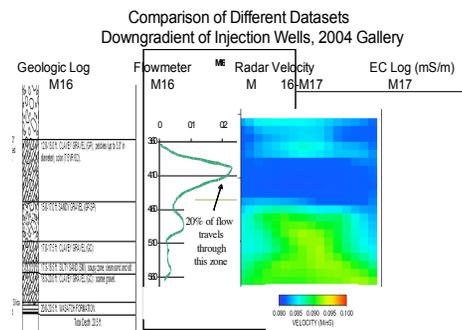


Figure B. Phase inversion results for the surface complex resistivity data acquired at using two frequencies and three time intervals with orientation as indicated; both the injection gallery boreholes and the monitoring well locations are indicated and refer to the locations shown in Fig. A. Per convention, the phase values shown are plotted as their negative value in milliradians, with the scale expanded for the data collected parallel to groundwater flow to enhance temporal changes in the phase response. The red boxes illustrate our hypothesis that mixing between the two galleries occurred, possibly due to the impact of preferential flowpaths on the transformations.

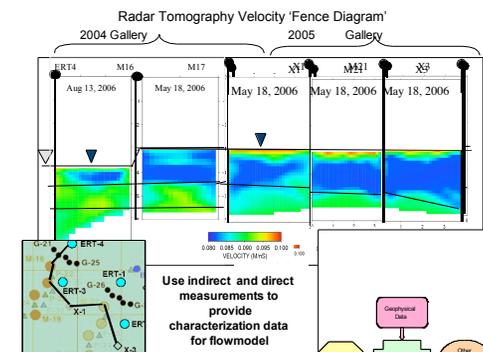


Figure C. Example of the 2005 phase inversion results for 0.125 Hz surface complex resistivity data acquired perpendicular to flow for comparison with Figure B. Acetate amendment during the 2005 experiment was limited to 25-days and no parallel injection was performed in the '2004' gallery location. Stimulation of iron-reduction in the '2004' gallery during the 2006 experiment may have contributed to the elevated phase response relative to the phase shifts observed in 2005.

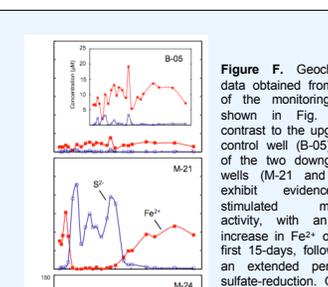
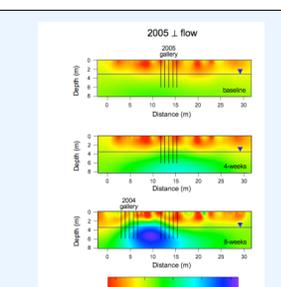
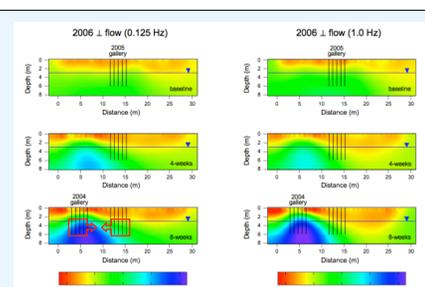
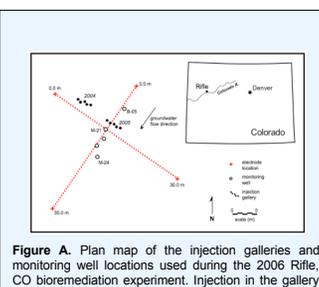
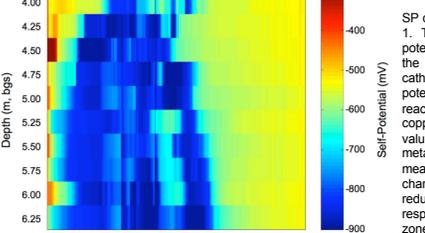
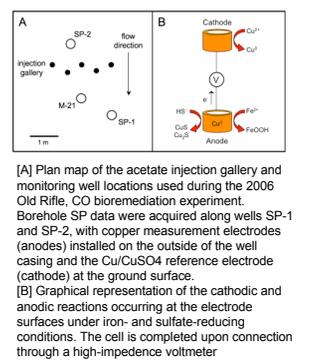
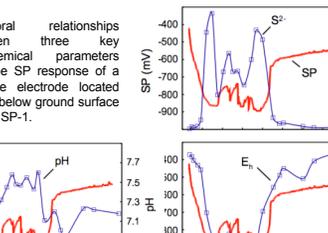


Figure F. Geochemical data obtained from three of the monitoring wells shown in Fig. A. In contrast to the upgradient control well (B-05), each of the two downgradient wells (M-21 and M-24) exhibit evidence of stimulated microbial activity, with an initial increase in Fe^{2+} over the first 15-days, followed by an extended period of sulfate-reduction. Of note, removal of Fe^{2+} during the onset and duration of sulfate-reduction is likely reflective of precipitation and sequestration of insoluble FeS.



SP data acquired along well SP-1. The magnitude of the cell potential can be estimated using the difference between the cathodic and anodic half-cell potentials, with a given anodic reaction (e.g. sulfide-mediated copper-oxidation) yielding a value reflective of the dominant metabolic process. Here, the measured potentials are characteristic of sulfate-reduction dominating the response downgradient from the zone of acetate injection.



The surface complex resistivity data shown in Figure B were collected at 30- and 67-days.